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(54) COMPOSITION FOR FORMING TITANIUM OXIDE MEMBRANE AND PHOTOCATALYST STRUCTURE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a well-balanced membrane forming compsn. having excellent photocatalytic activity and having both of excellent optical characteristics and mechanical durability by allowing a titanium oxide sol and stabilized titanium alkoxide to coexist.

SOLUTION: Titanium oxide particles obtained by hydrolyzing a titanyl sulfate soln. are filtered and washed to be dispersed in a nitric acid aq. soln. to obtain an anatase titanium oxide sol. Triethylene glycol is added to tetrapropoxytitanium at room temp. under stirring and, after reaction, acetyl acetone is added to the reaction soln. to be reacted with the reaction product and ethyl alcohol is added to the reaction soln. to be mixed therewith to obtain stabilized titanium alkoxide. A mixed solvent of ethyl alcohol and ethyl acetate is added to the titanium oxide sol to be uniformly dispersed and, thereafter, stabilized titanium alkoxide is dripped to the resulting dispersion little by little while mixed to be uniformly mixed therewith to prepare a titanium oxide membrane forming compsn. This titanium oxide membrane forming compsn. is applied to the surface of a heat-resistant substrate to obtain a photocatalyst structure.

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CLAIMS

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[Claim(s)]

[Claim 1] The constituent for titanium oxide thin film formation which comes to contain a titanium oxide sol and a stabilization titanium alkoxide [claim 2] The constituent for titanium oxide thin film formation of claim 1 \*\*\*\*\* whose mean particle diameter of a titanium oxide sol is 50nm or less [claim 3] The constituent for titanium oxide thin film formation according to claim 1 or 2 whose deflocculant of a titanium oxide sol is a nitric acid [claim 4] The constituent for titanium oxide thin film formation according to claim 1 to 3 whose dispersant of a titanium oxide sol is a water solution containing an alcoholic system organic solvent [claim 5] The constituent for titanium oxide thin film formation according to claim 1 to 4 whose stabilizing agents of a stabilization titanium alkoxide are one sort or two sorts or more of organic compounds which can form titanium and a chelate ring [claim 6] The constituent for titanium oxide thin film formation according to claim 1 to 5 whose stabilizing agents of a stabilization titanium alkoxide are glycols and/or beta-diketones [claim 7] The constituent for titanium oxide thin film formation according to claim 1 to 6 whose titanium oxide contents of the titanium oxide sol origin are 5 of the total amount of titanium oxide thru/or 60 % of the weight [claim 8] The photocatalyst structure which comes to support the constituent for titanium oxide thin film formation which comes to contain a titanium oxide sol and a stabilization titanium alkoxide on a heat-resistant base front face [claim 9] The photocatalyst structure according to claim 8 made to support by applying to a heat-resistant base front face the constituent for titanium oxide thin film formation which comes to contain a titanium oxide sol and a stabilization titanium alkoxide, and calcinating it at the temperature of 350 degrees C thru/or 750 degrees C [claim 10] The photocatalyst structure according to claim 8 or 9 to which a heat-resistant base is characterized by being a glass base

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

## [0001]

[Field of the Invention] This invention relates to the photocatalyst structure using the constituent for titanium oxide thin film formation and it which make it possible to prepare the titanium oxide thin film which has the outstanding photocatalyst activity and has the outstanding optical property, mechanical endurance (light permeability etc.) (adhesion, a degree of hardness, wear nature, etc.), chemical durability (a water resisting property, acid-proof, alkalinity, etc.), etc. in a heat-resistant base front face.

## [0002]

[Description of the Prior Art] If light is irradiated from the former, the photocatalyst in which the deodorization function by adsorption and disassembly of a malodorous substance, the antifouling function by oxidization and decomposition of the quality of an organic contamination affix, and a sterilization function are shown will be known well, and many especially attempts using titanium oxide are reported. The base material of the shape of the shape of porosity which consists of various ingredients, the shape of a honeycomb, and a sheet is made to support the impalpable powder of titanium oxide about deodorization of a malodorous substance, and many approaches of irradiating ultraviolet rays at this are adopted. As the approach of supporting titanium oxide impalpable powder to various base materials, \*\* Make an volatile organic solvent etc. suspend titanium oxide impalpable powder, and to a base material, dry, spreading or after carrying out impregnation. To \*\* base material in which titanium oxide impalpable powder is made to mix in the manufacture process of each base material, \*\* A water soluble polymer, Paste up titanium oxide impalpable powder using organic system adhesives and inorganic system adhesives. \*\* After dipping base materials, such as a nonwoven fabric, in the constituent which consists of a titanium alkoxide and titanium oxide impalpable powder, a titanium alkoxide is hydrolyzed and the approach (JP,4-174679,A) of drying at the temperature of about 150 degrees C is proposed. By these approaches, the great portion of titanium oxide impalpable powder with the weak (\*\*, \*\*, \*\*) adhesive strength of titanium oxide impalpable powder and a base material is incorporated in a base material, and the titanium oxide on the front face of a base material has faults, such as little (\*\*) etc. Furthermore, since it aims at deodorization, the specific surface area of titanium oxide impalpable powder is maximized, and since it is made the front face to which a malodorous substance tended to stick, a pollutant tends to adhere to reverse.

[0003] On the other hand, about antifouling or antibacterial, \*\* titanium oxide impalpable powder is sprayed on a hot tile front face etc., and it sinters at an elevated temperature (JP,5-253544,A), \*\* the alcoholic solution of \*\* titanium alkoxide which applies to a glass substrate the constituent which added the polyethylene glycol (average molecular weight 20,000) to the titanium oxide sol, and calcinates it at 450 degrees C (JP,7-51646,A) — a hydrochloric acid and diisopropanolamine — adding — transparent sol liquid — preparing — DIPPUKO-TINGU — membranes are formed to a glass substrate by law, and it calcinates at 630 degrees C — etc. (JP,7-100378,A) etc. — the approach is proposed. However, by these approaches, although antifouling property and antibacterial are high, since the titanium oxide film is translucent, although the light transmittance with low (\*\*, \*\*) light transmittance is high, it has troubles, such as (\*\*) etc. with bad stability of presentation liquid and membranous adhesion.

## [0004]

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the constituent for thin film formation which maintained the balance which has the outstanding photocatalyst activity and has the outstanding optical property, mechanical endurance (light permeability etc.) (adhesion, a degree of hardness, wear nature, etc.), and chemical durability (a water resisting property, acid-proof, alkalinity, etc.). Moreover, other objects of this invention are to have the optical property which formed the titanium oxide thin film to the glass base, and was excellent in it, mechanical endurance, and chemical durability, and offer the efficient antifouling property (self-consecration nature) photocatalyst structure.

## [0005]

[Means for Solving the Problem] As a result of advancing research wholeheartedly that this object should be attained, by making a titanium oxide sol and a stabilization titanium alkoxide live together, this invention persons find out that the alcoholic content water solution which distributed the titanium oxide sol stably over the long period of time is obtained, examine a titanium oxide thin film with high optical property which was excellent based on this knowledge, mechanical endurance and chemical durability, and photocatalyst activity, and came to complete this invention.

[0006] The constituent for titanium oxide thin film formation applied to this invention in order to solve the above-mentioned technical problem (Configuration 1) It considers as the presentation which comes to contain a titanium oxide sol and a stabilization titanium alkoxide. As a mode of this configuration 1 (Configuration 2) The mean particle diameter of said titanium oxide sol considers as the configuration which is 50nm or less. As a configuration 1 or a mode of 2 (Configuration 3) The deflocculant of said titanium oxide sol considers as the configuration which is a nitric acid. As a mode of a configuration 1 thru/or either of 3 (Configuration 4) It considers as the configuration whose dispersant of said titanium oxide sol is a water solution containing an alcoholic system organic solvent. As another mode of a configuration 1 thru/or either of 4 (Configuration 5) It considers as the configuration whose stabilizing agents of said stabilization titanium alkoxide are one sort or two sorts or more of organic compounds which can form titanium and a chelate ring. As a mode of a configuration 5 (Configuration 6) The stabilizing agent of said stabilization titanium alkoxide considers as the configuration which are glycols and/or beta-diketones. As a mode of a configuration 1 thru/or either of 6 (Configuration 7) The titanium oxide content of said titanium oxide sol origin considers as the configuration which are 5 of the total amount of titanium oxide thru/or 60 % of the weight. Moreover, the photocatalyst structure concerning this invention (configuration 8) It considers as the configuration which comes to support said constituent for titanium oxide thin film

formation on a heat-resistant base front face. As a mode of a configuration 8 (Configuration 9) Said constituent for titanium oxide thin film formation is applied to a heat-resistant base front face, and it considers as the configuration which was calcinated and was made to support with the temperature of 350 degrees C thru/or 750 degrees C, and is a configuration 8 thru/or a mode of 9. (configuration 10) Said heat-resistant base considers as the configuration characterized by being a glass base.

[0007]

[Embodiment of the Invention] According to the above-mentioned configuration 1, it became possible to obtain the antifouling property photocatalyst structure with the outstanding optical property, mechanical endurance and sufficient chemical durability, and sufficient effectiveness by obtaining the alcoholic content water solution which distributed the titanium oxide sol stably over the long period of time, using this constituent, and applying and calcinating at a glass base.

[0008] According to the configuration 2, it contributes to improvement in the stability of the constituent for titanium oxide thin film formation, and the improvement in light permeability of a titanium oxide thin film by setting mean particle diameter of titanium oxide to 50nm or less. The desirable still smaller one of mean particle diameter is good, and especially its about 5-10nm is desirable. This mean particle diameter computes X-ray particle size from the formula of Sheller. If mean particle diameter is set to 50nm or more, a titanium oxide particle will become easy to sediment and the permeability of a titanium oxide thin film will fall further.

[0009] According to the configuration 3, by using the deflocculant of a titanium oxide sol as a nitric acid, it can distribute stably, without condensing a titanium oxide particle, and photocatalyst activity can be further made high. Furthermore, it thinks because it does not remain in a thin film by the oxidation facilitatory effect of the organic substance, and volatilization in a baking process after applying a constituent with a stabilization titanium alkoxide to a glass base.

[0010] According to the configuration 4, it can distribute to stability, without a dispersant's mixing the organic solvent solution of the titanium oxide sol of water, and a stabilization titanium alkoxide to homogeneity, and sedimenting a titanium oxide sol.

[0011] According to the configuration 5, sedimentation of the rapid hydrolysis prevention and the titanium oxide particle of a titanium alkoxide by the water in a titanium oxide sol can be prevented by using the titanium alkoxide stabilized using the organic compound (henceforth a chelating agent) which can form titanium and a chelate ring. As an organic compound which can form titanium and a chelate ring, for example alpha-, such as beta-diketones, such as an acetylacetone and a benzoylacetone, an acetoacetic acid, and a propionyl acetic acid, Or low-grade alkyl ester, such as methyl of beta-keto acids and keto acids, ethyl, propyl, and butyl It is low-grade alkyl ester, such as oxy acid, such as a glycolic acid and a lactic acid, methyl of oxy acid, ethyl, propyl, and butyl, diols, and amino alcohol, and not only one sort but two sorts or more may be mixed and used.

[0012] In this invention, titanium alkoxides are titanium alkoxides expressed with  $Ti(OR)_4$ , for example, are a tetramethoxy red sandal tree, tetra-ethoxy titanium, tetraisopropoxy titanium, tetrabutoxytitanium, diethoxy diisopropoxytitanium, dimethoxy dibutoxy titanium, etc. The total number of mols of the chelating agent added to per one mol of titanium alkoxides is one mols or more, and is two mols or more preferably. Moreover, when using a chelating agent together with alcohols and using it, even if it carries out large superfluous addition, it does not interfere.

[0013] According to the configuration 6, especially, sedimentation of the rapid hydrolysis prevention and the titanium oxide particle of a titanium alkoxide by the water in a titanium oxide sol can be prevented preferably, and is further contributed to the improvement in the photocatalyst activity of the titanium oxide thin film applied and calcinated on the glass base, an optical property, mechanical endurance, etc.

$Ti(OR)_4 + 2(AA) \rightarrow Ti(-AA-)_2(-OR-)_2$  (however, AA shows an acetylacetone) — having generated —  $Ti(-AA-)_2(-OR-)_2$  (it is written as TAA) — In isopropyl alcohol coexistence-ization, since water solubility is shown and a solution shows the about five-PH ascence, the stability of a titanium oxide sol and titanium alkoxide dispersion liquid is raised by adding further water-soluble suitable glycols.

[0014] In this invention, the glycols of a liquid of especially glycols are desirable in ordinary temperature at water solubility. For example, carry out ring breakage of the alkylene oxide, such as ethylene oxide, propylene oxide, and butylene oxide, with water, and are obtained. For example, the polyalkylene glycol obtained by carrying out the polymerization of alkylene glycol and alkylene oxide, such as ethylene glycol, propylene glycol, and a butylene glycol, For example, the polymerization object of alkylene oxide, such as a diethylene glycol, triethylene glycol, a polyethylene glycol, polypropylene glycols, and those copolymers, is included. the mol of the glycols added to per one mol of titanium alkoxides — the mol of a number (G mols) and beta-diketones — the total number of mols of a number (K mols) is one mols or more, and is two mols or more preferably. Although the rate of G and K changes with descriptions of the total number of mols, and a titanium oxide sol, when the total number of mols is 2,  $G \geq 1$  and  $K \leq 1$  are desirable.

[0015] According to the configuration 7, although photocatalyst activity, an optical property, mechanical endurance, and chemical durability can be balanced, at 5 or less % of the weight, lack of photocatalyst activity is accompanied by lowering of the stability of a constituent, an optical property, a mechanical property, etc. by the titanium oxide content of the titanium oxide sol origin by 60 % of the weight or more. Furthermore, 15 - 40% of the weight of a titanium oxide content is good preferably.

[0016] According to a configuration 8 thru/or 9, the photocatalyst structure of the titanium oxide thin film of the outstanding photocatalyst activity and the outstanding optical property, mechanical endurance, and chemical durability is obtained by applying said constituent for titanium oxide thin film formation to a heat-resistant base, and calcinating it at 350 to 750 degrees C. Furthermore, preferably, by baking at 450 to 650 degrees C, a stabilization titanium alkoxide becomes the titanium oxide thin film of an anatase mold, and the outstanding photocatalyst activity is shown. Although baking by high temperature is desirable for mechanical endurance or the improvement in chemical durability, by baking at the temperature of 750 degrees C or more, a crystal mold turns into a rutile mold, the bottom of lowering of photocatalyst activity or nebula of a titanium oxide thin film starts, permeability falls, and it is not desirable. Moreover, in baking at the temperature of 350 degrees C or less, only that in which cannot become the titanium oxide thin film of an anatase mold easily, and mechanical endurance and chemical durability are also inferior is obtained.

[0017] Like a configuration 10 as a heat-resistant base, the property of the titanium oxide thin film of this invention will be further harnessed by using a glass base. That is, since permeability is high and photocatalyst activity also has it, the photocatalyst thin film concerning this invention can demonstrate the description enough, if the glass base of translucency is used as a base. [ high ] Moreover, if the cheap SODA lime glass currently used widely is used as a heat-resistant base, it is applicable to the aperture glass for transportation, such as aperture glass for buildings, an automobile, and an electric car, fluorescence tubing for lighting fitting, an electric bulb, front glass, a glass bookbinding object, etc.

[0018]

[Example]

After adding triethylene glycol 150g (one mol) in the <preparation of stabilization titanium alkoxide> reaction container and making it react to it at 70 degrees C for 30 minutes, teaching tetra-propoxytitanium 284g (one mol), and agitating under a room temperature, acetylacetone 100g (one mol) — adding — further — it was made to react for 30 minutes, and ethyl alcohol was added, it mixed to homogeneity, and the stabilization titanium alkoxide (A-1) whose titanium oxide content is about 5.0 % of the weight was obtained. Instead of triethylene glycol and an acetylacetone, two mols of independent [ of an acetylacetone, octylene glycol, and each triethanolamine ] were added, and also A-2, A-3, and A-4 were prepared like A-1. Moreover, equivalent mixture of A-2 and A-3 was set to A-5.

[0019] The titanium oxide particle which hydrolyzed and obtained the <preparation of titanium oxide sol> sulfuric-acid titanyl solution was distributed in the nitric-acid water solution after filtration and washing, and the titanium oxide sol (B-1) of the anatase mold of 30 % of the weight of titanium oxide contents was obtained by PH about 1.5 and about 7nm of average particle systems. Gel was produced, rinsing filtration was carried out, aging processing was carried out in the autoclave after dilution with water, and the anatase mold titanium oxide sol (B-2) of PH9 and about 20nm of average particle systems was obtained from the titanium-tetrachloride water solution and the sodium bicarbonate water solution.

[0020] [The example of the constituent for titanium oxide thin film formation]

It is ethyl alcohol/to <example 1> titanium oxide sol (B-1) 50g. 100g of mixed solvents of ethyl acetate (50/50 % of the weight) was added, and homogeneity was distributed. It was dropped mixing stabilization titanium alkoxide (A-1) 1000g small quantity every to these dispersion liquid, it mixed to homogeneity, and the constituent for titanium oxide thin film formation (D-1) was prepared. The titanium oxide total amount in D-1 was about 6 % of the weight, and the titanium oxide content of the titanium oxide sol origin was 23.0% of the weight of the titanium oxide whole quantity.

[0021] The class of a <examples 2-5> titanium oxide sol and stabilization titanium alkoxide was changed, and the constituent D-2 to D-5 for titanium oxide thin film formation was prepared like the example 1.

[0022] The constituent D-6 for titanium oxide thin film formation was prepared like the example 1 using the tetra-propoxytitanium which is not stabilized instead of the <example 1 of comparison> stabilization titanium alkoxide. Shortly after adding the titanium oxide sol, a lot of precipitate arose.

[0023] The presentation ratio of the constituent for titanium oxide thin film formation prepared in examples 1-6 and the example 1 of a comparison etc. was collectively shown in a table -1. Moreover, the change after keeping these constituents for one month at a room temperature was judged visually, and the stability was checked. The result was also doubled and it was shown in a table -1.

[0024]

[A table 1]

表 - 1

|                           | D - 1 | D - 2 | D - 3 | D - 4    | D - 5 | D - 6 |
|---------------------------|-------|-------|-------|----------|-------|-------|
| 安定化チタンアルキド                | A - 1 | A - 2 | A - 4 | A - 5    | A - 1 | 比較例   |
| 組成 (モル)                   |       |       |       |          |       |       |
| Ti (OR) <sub>4</sub>      | 1.0   | 1.0   | 1.0   | 2.0      | 1.0   | 1.0   |
| TEG                       | 1.0   |       |       |          | 1.0   |       |
| AA                        | 1.0   | 2.0   |       | 2.0      | 1.0   |       |
| OG                        |       |       |       | 2.0      |       |       |
| TEA                       |       |       | 2.0   |          |       |       |
| 酸化チタンゾル                   | B - 1 | B - 1 | B - 2 | B - 1    | B - 1 | B - 1 |
| 解膠剤                       | 硝酸    | 硝酸    | アルカリ  | 硝酸       | 硝酸    | 硝酸    |
| 粒径 (nm)                   | 7     | 7     | 20    | 7        | 7     | 7     |
| 酸化チタン中のゾル<br>系酸化チタン (wt%) | 23.0  | 37.5  | 10.0  | 50.0     | 5.0   | 23.0  |
| 安定性                       | 安定    | 安定    | 安定    | やや<br>分離 | 安定    | 沈殿多   |

TEG : トリエチレングリコール      AA : アセチルアセトン

OG : オクチレングリコール      TEA : トリエタノールアミン

[0025] [The example of the photocatalyst structure]

Membranes were formed with the dip method using the substrate which carried out precoat of about 100nm oxidation silicon thin film to soda lime glass using the constituent (D-1) prepared in the <example 7> example 1, it calcinated at 500 degrees C for 60 minutes, and anatase mold titanium oxide thin film glass of about 100nm of transparent thickness without nebula was obtained.

[0026] Using the constituent (D-1 to D-6) prepared in the <examples 8-13> examples 1-6, burning temperature and thickness were changed, and also the same actuation as an example 7 was performed, and titanium oxide support glass was created.

[0027] This film was nebula opacity, although titanium oxide powder was made to adhere with a dip method, it calcinated at 500 degrees C for 1 hour and titanium oxide support glass was created using the precoat glass same to D-6 prepared in the example 1 of a comparison which carried out the <example 2 of comparison> enforcement \*\*\*\* as an example 7.

[0028] The result of having measured the antifouling property, the light permeability, mechanical endurance, and chemical durability of the photocatalyst structure obtained in examples 7-13 and the example 2 of a comparison by the following approach was shown in a table -2.

[0029] The decomposition experiment of the salad oil of marketing which uses linolic acid as a principal component as an index of an antifouling functional measuring method antifouling function was conducted. In paper, thinly, salad oil was applied to the front face of the vitreous humour which attached the titanium oxide thin film so that it might be set to 0.1 to 0.15 mg per two 1cm. Coverage was calculated by the gravimetry before and behind spreading. In order to install the light of the ultraviolet-rays light containing a part of at least 200-400nm light so that it may become 3 mW/cm<sup>2</sup> in a glass body surface, and to ask for the relation between elapsed time and weight variation after an exposure, the weight of the vitreous humour in predetermined time was measured with the precision balance, and it considered as the index of decomposition activity. Antifouling property was ranked and carried out by the cracking severity of 8 hours after. A (90 - 100%), B (70 - 89%), C (50 - 69%), D (49% following)

The predetermined sample was installed in about 1l. reaction container, irradiating the ultraviolet rays of 1 mW/cm<sup>2</sup> after adhering the smoke of the tobacco of the specified quantity, change of a color was measured with the color difference meter, and the resolvability of the tar of tobacco was evaluated. Antifouling property was ranked and carried out by the cracking severity of 1 hour after. A (90 - 100%), B (70 - 89%), C (50 - 69%), D (49% following)

[0030] The predetermined sample was installed in the reaction container of about 1.5l. of deodorization functional measuring methods, after pouring in acetaldehyde gas so that the interior may become the concentration which is 1300 ppm, UV irradiation of 1.2 mW/cm<sup>2</sup> was performed, and the deodorization function was measured by concentration reduction. Antifouling property was ranked and carried out by the cracking severity of 1 hour after. A (90 - 100%), B (70 - 89%), C (50 - 69%), D (49% or less)

[0031] A part of vitreous humour which attached the measurement titanium oxide of optical straight-line transmission was cut, and the sample with a width of face [ of 10mm ] and a die length of 20mm was prepared. The same sample was prepared by the vitreous humour which has not attached titanium oxide, and the straight-line permeability to light with a wavelength of 550nm was measured with the Shimazu UV-3100PC spectrophotometer by making one of the two into a sample side and one of the two reference-side.

[0032] A pencil hardness test and wear nature performed mechanical endurance measuring method adhesion by the Scotch tape friction test, and performed the degree of hardness by the rubber abrasion test. Adhesion and wear nature considered what not exfoliating and the thing which is not worn out as acceptance.

[0033] The ebullition-proof [ chemical durability examining method ] water test is JIS. It is K5400, an alkali resistant test uses a 0.05%NaOH water solution, and it is JIS. According to the approach of K5400, it dipped for 24 hours and examined.

[0034]

表-2

| 実施例 | 組成物<br>番号 | 焼成<br>温度 | 膜厚<br>(nm) | 透過率<br>(%) | 防汚性 | 密着性 | 硬度 | 耐煮<br>沸性 | 耐アル<br>カリ性 |
|-----|-----------|----------|------------|------------|-----|-----|----|----------|------------|
| 7   | D-1       | 500      | 100        | 85         | A   | 合格  | 6H | 合格       | 合格         |
| 8   | D-1       | 500      | 50         | 80         | B   | 合格  | 7H | 合格       | 合格         |
| 9   | D-1       | 650      | 150        | 90         | A   | 合格  | 6H | 合格       | 合格         |
| 10  | D-2       | 500      | 100        | 88         | A   | 合格  | 5H | 合格       | 合格         |
| 11  | D-3       | 600      | 50         | 70         | C   | 合格  | 7H | 合格       | 合格         |
| 12  | D-4       | 500      | 50         | 80         | A   | 合格  | 4H | 合格       | 合格         |
| 13  | D-5       | 550      | 200        | 75         | B   | 合格  | 6H | 合格       | 合格         |

[0035] From the result of a table -2, the titanium oxide thin film glass of an example 7 had the optical property which 85% of light permeability, A ranks of antifouling property, pencil degree-of-hardness 6H and adhesion, boiling water resistance, and whose alkali resistance are acceptance, and was excellent, mechanical endurance, and chemical durability, and it was the photocatalyst structure of efficient antifouling property. Moreover, 70% or more of light permeability, more than pencil degree-of-hardness 4H and adhesion, boiling water resistance, and alkali resistance were acceptance, and the titanium oxide thin film glass of examples 8-13 also had the outstanding optical property, mechanical endurance, and chemical durability, and was the photocatalyst structure of efficient antifouling property.

[0036] The adhesion of the tar of tobacco, the resolvability of tar, and the deodorization nature of an acetaldehyde were compared, and the titanium oxide thin film created in the <photocatalyst activity trial> example 7, the example 13, and the example 2 of a comparison was shown in a table -3.

[0037]

表-3

| 実施例                   | 13  | 7    | 比較例2 |
|-----------------------|-----|------|------|
| ゾル系酸化チタン<br>含量 (wt %) | 5.0 | 23.0 | 100  |
| 膜厚 (nm)               | 200 | 100  | 500  |
| 透明性                   | 透明  | 透明   | 白濁   |
| 密着性                   | 合格  | 合格   | 不合格  |
| 煙草ヤニの付着性              | 小   | 小    | 大    |
| 煙草ヤニの分解性              | B   | A    | A    |
| アセトアルデヒド<br>の消臭性      | C   | B    | A    |

[0038] Although the film front face of the example 2 of a comparison has dramatically large surface area at porosity, and it is easy to adsorb the tar of a cigarette and suitable for decomposition and deodorization of the resolvability of tar, or an acetaldehyde, the film front face is cloudy, and since membranous adhesion is also weak, it cannot be used for the equipment which contacts by hand the application which needs the permeability of light, and a film front face. On the other hand, the dirt which was dirt-hard and adhered has the self-consecration nature which can be decomposed immediately, and is transparent and excellent also in endurance with examples 7 and 13. Especially the example 7 is the photocatalyst structure which maintained the balance well. Moreover, these titanium oxide thin film glass was what the origin of the light of the usual white fluorescent lamp also has disinfectant [ over Escherichia coli ], and can use it effectively by the hospital, food industry, etc.

[0039] The same actuation as an example 1 was performed for the titanium oxide thin film constituent (D-1) which created about 100nm oxidization silicon thin film on the front glass of the high-pressure mercury-vapor lamp equipment of <example 14> 360W by the method of dipping / calcinating, and was used for it in the example 1 on it, about 200nm anatase mold titanium oxide thin film was formed, and the titanium oxide thin film glass for mercury-vapor lamps was created. The dirt by conventional front glass and the exhaust gas of a vehicle was compared for four months in the tunnel, using this titanium oxide thin film glass as front glass for high-speed street lighting. The direction which used glass conventionally was dirty, although 24% of illuminance lowering was accepted, the glass using a titanium oxide thin film also had little dirt, and the illuminance lowering by dirt is 6%, and showed the outstanding antifouling property.

[0040]

[Effect of the Invention] The constituent for titanium oxide thin film formation of this invention is the the best for having the photocatalyst activity which was excellent by being able to save at the stability after preparation and using the constituent for titanium oxide thin film formation of this invention, and the outstanding optical property, mechanical endurance, chemical durability, etc. being able to offer the well-balanced titanium oxide thin film photocatalyst structure, and using for high permeability and outdoor type lighting fitting for which antifouling property ability is needed especially.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the photocatalyst structure using the constituent for titanium oxide thin film formation and it which make it possible to prepare the titanium oxide thin film which has the outstanding photocatalyst activity and has the outstanding optical property, mechanical endurance (light permeability etc.) (adhesion, a degree of hardness, wear nature, etc.), chemical durability (a water resisting property, acid-proof, alkalinity, etc.), etc. in a heat-resistant base front face.

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[Translation done.]



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PRIOR ART

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[Description of the Prior Art] If light is irradiated from the former, the photocatalyst in which the deodorization function by adsorption and disassembly of a malodorous substance, the antifouling function by oxidization and decomposition of the quality of an organic contamination affix, and a sterilization function are shown will be known well, and many especially attempts using titanium oxide are reported. The base material of the shape of the shape of porosity which consists of various ingredients, the shape of a honeycomb, and a sheet is made to support the impalpable powder of titanium oxide about deodorization of a malodorous substance, and many approaches of irradiating ultraviolet rays at this are adopted. As the approach of supporting titanium oxide impalpable powder to various base materials, \*\* Dry, after making an volatile organic solvent etc. suspend titanium oxide impalpable powder and applying or infiltrating a base material. To \*\* base material in which titanium oxide impalpable powder is made to mix in the manufacture process of each base material, \*\* A water soluble polymer, Paste up titanium oxide impalpable powder using organic system adhesives and inorganic system adhesives. \*\* After dipping base materials, such as a nonwoven fabric, in the constituent which consists of a titanium alkoxide and titanium oxide impalpable powder, a titanium alkoxide is hydrolyzed and the approach (JP,4-174679,A) of drying at the temperature of about 150 degrees C is proposed. By these approaches, the great portion of titanium oxide impalpable powder with the weak (\*\*, \*\*, \*\*) adhesive strength of titanium oxide impalpable powder and a base material is incorporated in a base material, and the titanium oxide on the front face of a base material has faults, such as little (\*\*) etc. Furthermore, since it aims at deodorization, the specific surface area of titanium oxide impalpable powder is maximized, and since it is made the front face to which a malodorous substance tended to stick, a pollutant tends to adhere conversely.

[0003] On the other hand, about antifouling or antibacterial, \*\* titanium oxide impalpable powder is sprayed on a hot tile front face etc., and it sinters at an elevated temperature (JP,5-253544,A), \*\* the alcoholic solution of \*\* titanium alkoxide which applies to a glass substrate the constituent which added the polyethylene glycol (average molecular weight 20,000) to the titanium oxide sol, and calcinates it at 450 degrees C (JP,7-51646,A) — a hydrochloric acid and diisopropanolamine — adding — transparent sol liquid — preparing — DIPPUKO-TINGU — membranes are formed to a glass substrate by law, and it calcinates at 630 degrees C — etc. (JP,7-100378,A) etc. — the approach is proposed. However, by these approaches, although antifouling property and antibacterial are high, since the titanium oxide film is translucent, although the light transmittance with low (\*\*, \*\*) light transmittance is high, it has troubles, such as (\*\*) etc. with bad stability of presentation liquid and membranous adhesion.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The constituent for titanium oxide thin film formation of this invention is the the best for having the photocatalyst activity which was excellent by being able to save at the stability after preparation and using the constituent for titanium oxide thin film formation of this invention, and the outstanding optical property, mechanical endurance, chemical durability, etc. being able to offer the well-balanced titanium oxide thin film photocatalyst structure, and using for high permeability and outdoor-type lighting fitting for which antifouling property ability is needed especially.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the constituent for thin film formation which maintained the balance which has the outstanding photocatalyst activity and has the outstanding optical property, mechanical endurance (light permeability etc.) (adhesion, a degree of hardness, wear nature, etc.), and chemical durability (a water resisting property, acid-proof, alkalinity, etc.). Moreover, other purposes of this invention are to have the optical property which formed the titanium oxide thin film to the glass base, and was excellent in it, mechanical endurance, and chemical durability, and offer the efficient antifouling property (self-consecration nature) photocatalyst structure.

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## MEANS

[Means for Solving the Problem] As a result of advancing research wholeheartedly that this purpose should be attained, by making a titanium oxide sol and a stabilization titanium alkoxide live together, this invention persons find out that the alcoholic content water solution which distributed the titanium oxide sol stably over the long period of time is obtained, examine a titanium oxide thin film with high optical property which was excellent based on this knowledge, mechanical endurance and chemical durability, and photocatalyst activity, and came to complete this invention.

[0006] The constituent for titanium oxide thin film formation applied to this invention in order to solve the above-mentioned technical problem (Configuration 1) It considers as the presentation which comes to contain a titanium oxide sol and a stabilization titanium alkoxide. As a mode of this configuration 1 (Configuration 2) The mean particle diameter of said titanium oxide sol considers as the configuration which is 50nm or less. As a configuration 1 or a mode of 2 (Configuration 3) The deflocculant of said titanium oxide sol considers as the configuration which is a nitric acid. As a mode of a configuration 1 thru/or either of 3 (Configuration 4) It considers as the configuration whose dispersant of said titanium oxide sol is a water solution containing an alcoholic system organic solvent. As another mode of a configuration 1 thru/or either of 4 (Configuration 5) It considers as the configuration whose stabilizing agents of said stabilization titanium alkoxide are one sort or two sorts or more of organic compounds which can form titanium and a chelate ring. As a mode of a configuration 5 (Configuration 6) The stabilizing agent of said stabilization titanium alkoxide considers as the configuration which are glycols and/or beta-diketones. As a mode of a configuration 1 thru/or either of 6 (Configuration 7) The titanium oxide content of said titanium oxide sol origin considers as the configuration which are 5 of the total amount of titanium oxide thru/or 60 % of the weight. Moreover, the photocatalyst structure concerning this invention (configuration 8) It considers as the configuration which comes to support said constituent for titanium oxide thin film formation on a heat-resistant base front face. As a mode of a configuration 8 (Configuration 9) Said constituent for titanium oxide thin film formation is applied to a heat-resistant base front face, and it considers as the configuration which was calcinated and was made to support with the temperature of 350 degrees C thru/or 750 degrees C, and is a configuration 8 thru/or a mode of 9. (configuration 10) Said heat-resistant base considers as the configuration characterized by being a glass base.

[0007]

[Embodiment of the Invention] According to the above-mentioned configuration 1, it became possible to obtain the antifouling property photocatalyst structure with the outstanding optical property, mechanical endurance and sufficient chemical durability, and sufficient effectiveness by obtaining the alcoholic content water solution which distributed the titanium oxide sol stably over the long period of time, using this constituent, and applying and calcinating at a glass base.

[0008] According to the configuration 2, it contributes to improvement in the stability of the constituent for titanium oxide thin film formation, and the improvement in light permeability of a titanium oxide thin film by setting mean particle diameter of titanium oxide to 50nm or less. The desirable still smaller one of mean particle diameter is good, and especially its about 5-10nm is desirable. This mean particle diameter computes X-ray particle size from the formula of Sheller. If mean particle diameter is set to 50nm or more, a titanium oxide particle will become easy to sediment and the permeability of a titanium oxide thin film will fall further.

[0009] According to the configuration 3, by using the deflocculant of a titanium oxide sol as a nitric acid, it can distribute stably, without condensing a titanium oxide particle, and photocatalyst activity can be further made high. Furthermore, it thinks because it does not remain in a thin film by the oxidation facilitatory effect of the organic substance, and volatilization in a baking process after applying a constituent with a stabilization titanium alkoxide to a glass base.

[0010] According to the configuration 4, it can distribute to stability, without a dispersant's mixing the organic solvent solution of the titanium oxide sol of water, and a stabilization titanium alkoxide to homogeneity, and sedimenting a titanium oxide sol.

[0011] According to the configuration 5, sedimentation of the rapid hydrolysis prevention and the titanium oxide particle of a titanium alkoxide by the water in a titanium oxide sol can be prevented by using the titanium alkoxide stabilized using the organic compound (henceforth a chelating agent) which can form titanium and a chelate ring. As an organic compound which can form titanium and a chelate ring, for example alpha-, such as beta-diketones, such as an acetylacetone and a benzoylacetone, an acetoacetic acid, and a propionyl acetic acid, Or low-grade alkyl ester, such as methyl of beta-keto acids and keto acids, ethyl, propyl, and butyl It is low-grade alkyl ester, such as oxy acid, such as a glycolic acid and a lactic acid, methyl of oxy acid, ethyl, propyl, and butyl, diols, and amino alcohol, and not only one sort but two sorts or more may be mixed and used.

[0012] In this invention, titanium alkoxides are titanium alkoxides expressed with  $Ti(OR)_4$ , for example, are a tetramethoxy red sandal tree, tetra-ethoxy titanium, tetraisopropoxy titanium, tetrabutoxytitanium, diethoxy diisopropoxytitanium, dimethoxy dibutoxy titanium, etc. The total number of mols of the chelating agent added to per one mol of titanium alkoxides is one mols or more, and is two mols or more preferably. Moreover, when using a chelating agent together with alcohols and using it, even if it carries out large superfluous addition, it does not interfere.

[0013] According to the configuration 6, especially, sedimentation of the rapid hydrolysis prevention and the titanium oxide particle of a titanium alkoxide by the water in a titanium oxide sol can be prevented preferably, and is further contributed to the improvement in the photocatalyst activity of the titanium oxide thin film applied and calcinated on the glass base, an optical property, mechanical endurance, etc.

$Ti(OR)_4 + 2(AA) \rightarrow Ti(-AA)_2$  — two — (— OR —) — two (however, AA shows an acetylacetone) — having generated —  $Ti(-AA)_2$  — two — (— OR —) — two (it is written as TAA) — In isopropyl alcohol coexistence-ization, since water solubility is shown and a solution shows the about five-PH ascence, the stability of a titanium oxide sol and titanium alkoxide dispersion liquid is raised by adding further water-soluble suitable glycols.

[0014] In this invention, the glycols of a liquid of especially glycols are desirable in ordinary temperature at water solubility. For example, carry out ring breakage of the alkylene oxide, such as ethylene oxide, propylene oxide, and butylene oxide, with water, and are obtained. For example, the polyalkylene glycol obtained by carrying out the polymerization of alkylene glycol and alkylene oxide, such as ethylene glycol, propylene glycol, and a butylene glycol. For example, the polymerization object of alkylene oxide, such as a diethylene glycol, triethylene glycol, a polyethylene glycol, polypropylene glycols, and those copolymers, is included. the mol of the glycols added to per one mol of titanium alkoxides — the mol of a number (G mols) and beta-diketones — the total number of mols of a number (K mols) is one mols or more, and is two mols or more preferably. Although the rate of G and K changes with descriptions of the total number of mols, and a titanium oxide sol, when the total number of mols is 2,  $G \geq 1$  and  $K \leq 1$  are desirable.

[0015] According to the configuration 7, although photocatalyst activity, an optical property, mechanical endurance, and chemical durability can be balanced, at 5 or less % of the weight, lack of photocatalyst activity is accompanied by the fall of the stability of a constituent, an optical property, a mechanical property, etc. by the titanium oxide content of the titanium oxide sol origin by 60 % of the weight or more. Furthermore, 15 – 40% of the weight of a titanium oxide content is good preferably.

[0016] According to a configuration 8 thru/or 9, the photocatalyst structure of the titanium oxide thin film of the outstanding photocatalyst activity and the outstanding optical property, mechanical endurance, and chemical durability is obtained by applying said constituent for titanium oxide thin film formation to a heat-resistant base, and calcinating it at 350 to 750 degrees C. Furthermore, preferably, by baking at 450 to 650 degrees C, a stabilization titanium alkoxide becomes the titanium oxide thin film of an anatase mold, and the outstanding photocatalyst activity is shown. Although baking by high temperature is desirable for mechanical endurance or the improvement in chemical durability, by baking at the temperature of 750 degrees C or more, a crystal mold turns into a rutile mold, the bottom of the fall of photocatalyst activity or nebula of a titanium oxide thin film starts, permeability falls, and it is not desirable. Moreover, in baking at the temperature of 350 degrees C or less, only that in which cannot become the titanium oxide thin film of an anatase mold easily, and mechanical endurance and chemical durability are also inferior is obtained.

[0017] Like a configuration 10 as a heat-resistant base, the property of the titanium oxide thin film of this invention will be further harnessed by using a glass base. That is, since permeability is high and photocatalyst activity also has it, the photocatalyst thin film concerning this invention can demonstrate the description enough, if the glass base of translucency is used as a base. [ high ] Moreover, if the cheap SODA lime glass currently used widely is used as a heat-resistant base, it is applicable to the aperture glass for transportation, such as aperture glass for buildings, an automobile, and an electric car, fluorescence tubing for lighting fitting, an electric bulb, front glass, a glass bookbinding object, etc.

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EXAMPLE

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[Example]

After adding triethylene glycol 150g (one mol) in the <preparation of stabilization titanium alkoxide> reaction container and making it react to it at 70 degrees C for 30 minutes, teaching tetra-propoxytitanium 284g (one mol), and agitating under a room temperature, acetylacetone 100g (one mol) — adding — further — it was made to react for 30 minutes, and ethyl alcohol was added, it mixed to homogeneity, and the stabilization titanium alkoxide (A-1) whose titanium oxide content is about 5.0 % of the weight was obtained. Instead of triethylene glycol and an acetylacetone, two mols of independent [ of an acetylacetone, octylene glycol, and each triethanolamine ] were added, and also A-2, A-3, and A-4 were prepared like A-1. Moreover, equivalent mixture of A-2 and A-3 was set to A-5.

[0019] The titanium oxide particle which hydrolyzed and obtained the <preparation of titanium oxide sol> sulfuric-acid titanyl solution was distributed in the nitric-acid water solution after filtration and washing, and the titanium oxide sol (B-1) of the anatase mold of 30 % of the weight of titanium oxide contents was obtained by PH about 1.5 and about 7nm of average particle systems. Gel was produced, rinsing filtration was carried out, aging processing was carried out in the autoclave after dilution with water, and the anatase mold titanium oxide sol (B-2) of PH9 and about 20nm of average particle systems was obtained from the titanium-tetrachloride water solution and the sodium bicarbonate water solution.

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最終頁に続く

(54) 【発明の名称】 酸化チタン薄膜形成用組成物及びそれを用いる光触媒構造体

(57) 【要約】

【課題】 優れた光触媒活性を有し、且つ、優れた光学特性、機械的耐久性及び化学的耐久性を併せ持つバランスのとれた薄膜形成用組成物を提供する。また、耐熱性基体に酸化チタン薄膜を成膜し、優れた光学特性、機械的耐久性及び化学的耐久性を有し、且つ、防汚活性の優れた光触媒構造体を提供する。

【解決手段】 本発明は、酸化チタンゾルと安定化チタンアルコキシドを含有してなる酸化チタン薄膜形成用組成物及びそれを耐熱性基体に担持してなる光触媒構造体である。

## 【特許請求の範囲】

【請求項 1】酸化チタンゾルと安定化チタンアルコキシドを含有してなる酸化チタン薄膜形成用組成物

【請求項 2】酸化チタンゾルの平均粒子径が、50 nm 以下である請求項 1 記載の酸化チタン薄膜形成用組成物

【請求項 3】酸化チタンゾルの解膠剤が、硝酸である請求項 1 又は 2 記載の酸化チタン薄膜形成用組成物

【請求項 4】酸化チタンゾルの分散剤が、アルコール系有機溶剤を含む水溶液である請求項 1 乃至 3 のいずれかに記載の酸化チタン薄膜形成用組成物

【請求項 5】安定化チタンアルコキシドの安定化剤が、チタンとキレート環を形成し得る 1 種又は 2 種以上の有機化合物である請求項 1 乃至 4 のいずれかに記載の酸化チタン薄膜形成用組成物

【請求項 6】安定化チタンアルコキシドの安定化剤が、グリコール類及び／又はβ-ジケトン類である請求項 1 乃至 5 のいずれかに記載の酸化チタン薄膜形成用組成物

【請求項 7】酸化チタンゾル由来の酸化チタン含量が、全酸化チタン量の 5 乃至 60 重量%である請求項 1 乃至 6 のいずれかに記載の酸化チタン薄膜形成用組成物

【請求項 8】酸化チタンゾルと安定化チタンアルコキシドを含有してなる酸化チタン薄膜形成用組成物を耐熱性基体表面に担持してなる光触媒構造体

【請求項 9】酸化チタンゾルと安定化チタンアルコキシドを含有してなる酸化チタン薄膜形成用組成物を耐熱性基体表面に塗布し、350℃乃至750℃の温度で焼成することにより担持させた請求項 8 記載の光触媒構造体

【請求項 10】耐熱性基体が、硝子基体であることを特徴とする請求項 8 又は 9 記載の光触媒構造体

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、優れた光触媒活性を有し、且つ、優れた光学特性（可視光透過率など）、機械的耐久性（密着性、硬度、磨耗性など）及び化学的耐久性（耐水性、耐酸・アルカリ性など）などを有する酸化チタン薄膜を耐熱性基体表面に設けることを可能にする酸化チタン薄膜形成用組成物及びそれを用いる光触媒構造体に関するものである。

## 【0002】

【従来の技術】従来から光を照射すると悪臭物質の吸着・分解による消臭機能、有機汚染付着物質の酸化・分解による防汚機能及び殺菌機能を示す光触媒は良く知られており、特に、酸化チタンを用いる試みは数多く報告されている。悪臭物質の消臭に関しては、酸化チタンの微粉末を各種材料からなる多孔質状、ハニカム状及びシート状の基材に担持させて、これに紫外線を照射する方法が多く採用されている。酸化チタン微粉末を各種基材に担持する方法としては、①酸化チタン微粉末を揮発性有機溶剤等に懸濁させ、基材に塗布または含浸させたのち

乾燥する、②各基材の製造過程で酸化チタン微粉末を混入させる、③基材に水溶性高分子、有機系接着剤、無機系接着剤を用いて酸化チタン微粉末を接着する、④チタンアルコキシド及び酸化チタン微粉末からなる組成物に不織布などの基材を浸漬した後、チタンアルコキシドを加水分解し、150℃程度の温度で乾燥する（特開平4-174679）などの方法が提案されている。これらの方法では、酸化チタン微粉末と基材との接着力が弱い（①、③、④）、酸化チタン微粉末の大部分が基材内に取り込まれて、基材表面の酸化チタンが少ない（②）などの欠点を有している。更に、消臭を目的としているため、酸化チタン微粉末の比表面積を最大化し、悪臭物質が吸着しやすい表面にしているため、逆に汚染物質が付着しやすい。

【0003】一方、防汚や抗菌に関しては、⑤酸化チタン微粉末を高温のタイル表面等に吹きつけて、高温で焼結する（特開平5-253544）、⑥酸化チタンゾルにポリエチレングリコール（平均分子量20,000）を添加した組成物を硝子基板に塗布し、450℃で焼成する（特開平7-51646）、⑦チタンアルコキシドのアルコール溶液に塩酸とジイソプロパノールアミンを加えて透明なゾル液を調製し、ディップコーティング法により硝子基板に成膜し、630℃で焼成する（特開平7-100378）などの方法が提案されている。しかし、これらの方法では、防汚性や抗菌性は高いが酸化チタン膜が半透明なため、光透過率が低い（⑤、⑥）、光透過率は高いが組成液の安定性や膜の密着性が悪い（⑦）などの問題点がある。

## 【0004】

【発明が解決しようとする課題】本発明の目的は、優れた光触媒活性を有し、且つ、優れた光学特性（可視光透過率など）、機械的耐久性（密着性、硬度、磨耗性など）及び化学的耐久性（耐水性、耐酸・アルカリ性など）を併せ持つバランスのとれた薄膜形成用組成物を提供することにある。また、本発明の他の目的は、硝子基体に酸化チタン薄膜を成膜し、優れた光学特性、機械的耐久性及び化学的耐久性を有し、且つ、効率のよい防汚性（自己浄化性）光触媒構造体を提供することにある。

## 【0005】

【課題を解決するための手段】本発明者らは、この目的を達成すべく鋭意研究を進めた結果、酸化チタンゾルと安定化チタンアルコキシドを共存させることにより、酸化チタンゾルを長期にわたって安定的に分散させたアルコール含有水溶液が得られることを見だし、この知見を基に優れた光学特性、機械的耐久性及び化学的耐久性と光触媒活性の高い酸化チタン薄膜の検討を行い、本発明を完成するに至った。

【0006】上記の課題を解決するために本発明にかかる酸化チタン薄膜形成用組成物は、（構成1）酸化チタンゾルと安定化チタンアルコキシドを含有してなる組



成とし、この構成 1 の態様として、(構成 2) 前記酸化チタンゾルの平均粒子径が、50 nm 以下である構成とし構成 1 又は 2 の態様として、(構成 3) 前記酸化チタンゾルの解膠剤が、硝酸である構成とし、構成 1 乃至 3 のいずれかの態様として、(構成 4) 前記酸化チタンゾルの分散剤が、アルコール系有機溶剤を含む水溶液である構成とし、構成 1 乃至 4 のいずれかの別の態様として、(構成 5) 前記安定化チタンアルコキシドの安定化剤が、チタンとキレート薬を形成し得る 1 種又は 2 種以上の有機化合物である構成とし、構成 5 の態様として、(構成 6) 前記安定化チタンアルコキシドの安定化剤が、グリコール類及び/または  $\beta$ -ジケトン類である構成とし、構成 1 乃至 6 のいずれかの態様として、(構成 7) 前記酸化チタンゾル由来の酸化チタン含量が、全酸化チタン量の 5 乃至 60 重量%である構成とし、また、本発明にかかる光触媒構造体は(構成 8) 前記酸化チタン薄膜形成用組成物を耐熱性基体表面に担持してなる構成とし構成 8 の態様として、(構成 9) 前記酸化チタン薄膜形成用組成物を耐熱性基体表面に塗布し、350℃乃至750℃の温度で焼成して担持せしめた構成とし、構成 8 乃至 9 の態様として、(構成 10) 前記耐熱性基体が、硝子基体であることを特徴とする構成としたものである。

#### 【0007】

【発明の実施の形態】上述の構成 1 によれば、酸化チタンゾルを長期にわたって安定的に分散させたアルコール含有水溶液が得られ、この組成物を用いて硝子基体に塗布・焼成することにより、優れた光学特性、機械的耐久性、及び化学的耐久性、効率のよい防汚性光触媒構造体を得ることが可能になった。

【0008】構成 2 によれば、酸化チタンの平均粒子径を 50 nm 以下にすることにより、酸化チタン薄膜形成用組成物の安定性の向上と酸化チタン薄膜の可視光透過性の向上に寄与する。平均粒子径は好ましくは更に小さいほうが良く、5~10 nm 程度が特に好ましい。この平均粒子径は、X線粒徑を *Shelley* の式より算出したものである。平均粒子径が 50 nm 以上になると酸化チタン微粒子が沈降しやすくなり、更に酸化チタン薄膜の透過率が低下する。

【0009】構成 3 によれば、酸化チタンゾルの解膠剤を硝酸にすることにより、酸化チタン微粒子を凝集することなく安定的に分散でき、更に光触媒活性を高くできる。さらに、安定化チタンアルコキシドとの組成物を硝子基体に塗布後、焼成過程において有機物の酸化促進効果と揮発によって薄膜中に残存しないためと考えられる。

【0010】構成 4 によれば、分散剤が水の酸化チタンゾルと安定化チタンアルコキシドの有機溶剤溶液を均一に混合して、酸化チタンゾルを沈降することなく安定に分散出来る。

【0011】構成 5 によれば、チタンとキレート薬を形成し得る有機化合物(以下、キレート化剤と言う)を使用して安定化したチタンアルコキシドを用いることにより、酸化チタンゾル中の水によるチタンアルコキシドの急速な加水分解防止と酸化チタン微粒子の沈降を防止出来る。チタンとキレート薬を形成し得る有機化合物としては、例えば、アセチルアセトン、ベンゾイルアセトン等の  $\beta$ -ジケトン類、アセト酢酸、プロピオニル酢酸等の  $\alpha$ -、または、 $\beta$ -ケト酸類、ケト酸類のメチル、エチル、プロピル、ブチル等の低級アルキルエステル類、グリコール酸、乳酸等のオキシ酸類、オキシ酸のメチル、エチル、プロピル、ブチル等の低級アルキルエステル類、ジオール類、アミノアルコール類などであり、1 種だけでなく 2 種以上を混合して用いてもよい。

【0012】本発明において、チタンアルコキシドとは、 $Ti(OR)_4$  で表されるチタンアルコキシド類であり、例えば、テトラメトキシチタン、テトラエトキシチタン、テトライソプロポキシチタン、テトラブトキシチタン、ジエトキシジイソプロポキシチタン、ジメトキシジブトキシチタン等である。チタンアルコキシド 1 モル当たりに添加するキレート化剤の総モル数は、1 モル以上で、好ましくは 2 モル以上である。また、キレート化剤をアルコール類と併用して用いるときは、大過剰添加しても差し支えない。

【0013】構成 6 によれば、酸化チタンゾル中の水によるチタンアルコキシドの急速な加水分解防止と酸化チタン微粒子の沈降を特に好ましく防止出来、更に、硝子基体上に塗布・焼成した酸化チタン薄膜の光触媒活性と光学特性、機械的耐久性などの向上に寄与する。

30  $Ti(OR)_4 + 2(AA) \rightarrow Ti(AA)_2(OR)_2$ ;  
(但し、AA はアセチルアセトンを示す)で生成した  $Ti(AA)_2(OR)_2$  (TAA と略記する) は、イソプロピルアルコール共存化では、水溶性を示し、溶液は pH 5 程度の弱酸性を示すので、好適であり更に、水溶性のグリコール類を添加することにより、酸化チタンゾルとチタンアルコキシド分散液の安定性を向上させる。

【0014】本発明において、グリコール類は、水溶性で常温で液体のグリコール類が特に好ましく、例えば、エチレンオキシド、プロピレンオキシド、ブチレンオキシドなどのアルキレンオキシドを水で開環して得られる、例えば、エチレングリコール、プロピレングリコール、ブチレングリコール等のアルキレングリコール及びアルキレンオキシドを重合して得られるポリアルキレングリコール、例えば、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール、ポリプロピレングリコール、それらの共重合体等のアルキレンオキシドの重合物を含む。チタンアルコキシド 1 モル当たりに添加するグリコール類のモル数(Gモル)と  $\beta$ -ジケトン類のモル数(Kモル)の総モル数は、1 モル以上  
50 で、好ましくは、2 モル以上である。G と K の割合は、

総モル数、酸化チタンゾルの性状によって異なるが、総モル数が 2 の時、 $G \geq 1$ 、 $K \leq 1$  が好ましい。

【0015】構成 7 によれば、光触媒活性と光学特性、機械的耐久性及び化学的耐久性のバランスを取ることが出来るが、酸化チタンゾル由来の酸化チタン含量が、5 重量%以下では光触媒活性の不足が、60 重量%以上では、組成物の安定性、光学特性及び機械的特性などの低下を伴う。更に好ましくは、15～40 重量%の酸化チタン含量が良い。

【0016】構成 8 乃至 9 によれば、前記酸化チタン薄膜形成用組成物を耐熱性基体に塗布し、350℃から 750℃で焼成することにより、優れた光触媒活性、光学特性、機械的耐久性及び化学的耐久性の酸化チタン薄膜の光触媒構造体を得る。更に好ましくは、450℃から 650℃での焼成により、安定化チタンアルコキシドが、アナターゼ型の酸化チタン薄膜になり、優れた光触媒活性を示す。機械的耐久性や化学的耐久性向上のためには、高温での焼成が好ましいが、750℃以上の温度での焼成により、結晶型がルチル型になり、光触媒活性の低下や酸化チタン薄膜の白濁下が始まり、透過率が低下し、好ましくない。又、350℃以下の温度での焼成では、アナターゼ型の酸化チタン薄膜になりにくく、かつ機械的耐久性や化学的耐久性も劣るものしか得られない。

【0017】耐熱性基体として構成 10 のように、硝子基体を使用することにより、本発明の酸化チタン薄膜の特性は一層活かされることになる。即ち、本発明にかかる光触媒薄膜は透過率が高く光触媒活性も高いものであるため、基体として透光性の硝子基体を使用すれば、その特徴を充分発揮することが出来る。また、汎用されている安価なソーダライム硝子などを耐熱性基体として使用すると、建築物用窓硝子、自動車、電車等の輸送機関用の窓硝子、照明器具用の蛍光管、電球、前面硝子および硝子製本体などへ応用することができる。

【0018】

【実施例】

<安定化チタンアルコキシドの調製>反応容器に、テトラプロポキシチタン 284 g (1 モル) を仕込み、室温下で攪拌しながらトリエチレングリコール 150 g (1 モル) を添加し、70℃で 30 分反応させたあと、アセチルアセトン 100 g (1 モル) を添加し、更に 30 分反応させ、エチルアルコールを添加して均一に混合し、

酸化チタン含量が約 5.0 重量%の安定化チタンアルコキシド (A-1) を得た。トリエチレングリコール及びアセチルアセトンの代わりに、アセチルアセトン、オクチレングリコール及びトリエタノールアミンそれぞれの単独を 2 モル添加した他は、A-1 と同様にして、A-2、A-3、A-4 を調製した。又、A-2 と A-3 の等量混合物を A-5 とした。

【0019】<酸化チタンゾルの調製>硫酸チタニル溶液を加水分解して得た酸化チタン粒子を濾過、洗浄後、硝酸水溶液で分散させ、PH 約 1.5、平均粒子系約 7 nm で、酸化チタン含量 30 重量%のアナターゼ型の酸化チタンゾル (B-1) を得た。四塩化チタン水溶液と重炭酸ナトリウム水溶液から、ゲルを作製、水洗濾過し、水で希釈後、オートクレーブ中で熟成処理して、PH 9、平均粒子系約 20 nm のアナターゼ型酸化チタンゾル (B-2) を得た。

【0020】〔酸化チタン薄膜形成用組成物の実施例〕

<実施例 1>酸化チタンゾル (B-1) 50 g にエチルアルコール/酢酸エチル (50/50 重量%) の混合溶媒 100 g を添加し、均一に分散させた。この分散液に安定化チタンアルコキシド (A-1) 1000 g を少量ずつ混合しながら滴下し、均一に混合して、酸化チタン薄膜形成用組成物 (D-1) を調製した。D-1 中の酸化チタン総量は、約 6 重量%であり、酸化チタンゾル由来の酸化チタン含量は酸化チタン全量の 23.0 重量%であった。

【0021】<実施例 2～5>酸化チタンゾルおよび安定化チタンアルコキシドの種類を変えて、実施例 1 と同様にして、酸化チタン薄膜形成用組成物 D-2～D-5 を調製した。

【0022】<比較例 1>安定化チタンアルコキシドの代わりに安定化していないテトラプロポキシチタンを用いて、実施例 1 と同様にして酸化チタン薄膜形成用組成物 D-6 を調製した。酸化チタンゾルを添加するとすぐに多量の沈殿物が生じた。

【0023】実施例 1～6 および比較例 1 で調製した酸化チタン薄膜形成用組成物の組成比等を表-1 にまとめて示した。また、これらの組成物を室温にて 1 ヶ月保管した後の変化を目視にて判定しその安定性を確認した。その結果も合わせて表-1 に示した。

【0024】

【表 1】

表 - 1

|                       | D - 1 | D - 2 | D - 3 | D - 4 | D - 5 | D - 6 |
|-----------------------|-------|-------|-------|-------|-------|-------|
| 安定化チタン粉組成 (モル)        | A - 1 | A - 2 | A - 4 | A - 5 | A - 1 | 比較例   |
| Ti (OR) <sub>4</sub>  | 1.0   | 1.0   | 1.0   | 2.0   | 1.0   | 1.0   |
| TEG                   | 1.0   |       |       |       | 1.0   |       |
| AA                    | 1.0   | 2.0   |       | 2.0   | 1.0   |       |
| OG                    |       |       |       | 2.0   |       |       |
| TEA                   |       |       | 2.0   |       |       |       |
| 酸化チタンゾル               | B - 1 | B - 1 | B - 2 | B - 1 | B - 1 | B - 1 |
| 解膠剤                   | 硝酸    | 硝酸    | アルカリ  | 硝酸    | 硝酸    | 硝酸    |
| 粒径 (nm)               | 7     | 7     | 20    | 7     | 7     | 7     |
| 酸化チタン中のゾル系酸化チタン (wt%) | 23.0  | 37.5  | 10.0  | 50.0  | 5.0   | 23.0  |
| 安定性                   | 安定    | 安定    | 安定    | やや分離  | 安定    | 沈殿多   |

TEG : トリエチレングリコール

AA : アセチルアセトン

OG : オクチレングリコール

TEA : トリエタノールアミン

## 【 0 0 2 5 】 [ 光触媒構造体の実施例 ]

< 実施例 7 > 実施例 1 で調製した組成物 ( D - 1 ) を用いて、ソーダ石灰硝子に約 1 0 0 n m の酸化珪素薄膜をプレコートした基板を用いて、ディップ法にて成膜し 5 0 0 ° C で 6 0 分焼成し、白濁のない透明な膜厚約 1 0 0 n m のアナターゼ型酸化チタン薄膜硝子を得た。

【 0 0 2 6 】 < 実施例 8 ~ 1 3 > 実施例 1 ~ 6 で調製した組成物 ( D - 1 ~ D - 6 ) を用いて、焼成温度、膜厚を変えた他は実施例 7 と同様の操作を行い、酸化チタン担持硝子を作成した。

【 0 0 2 7 】 < 比較例 2 > 強制攪拌した比較例 1 で調製した D - 6 に実施例 7 と同様のプレコート硝子を用いて、ディップ法にて酸化チタン粉末を付着させ、5 0 0 ° C で 1 時間焼成し、酸化チタン担持硝子を作成したがこの膜は白濁不透明であった。

【 0 0 2 8 】 実施例 7 ~ 1 3 および比較例 2 で得られた光触媒構造体の防汚性、可視光透過性、機械的耐久性及び化学的耐久性を下記の方法で測定した結果を表 - 2 に示した。

## 【 0 0 2 9 】 防汚機能測定法

防汚機能の指標としてリノール酸を主成分とする市販のサラダ油の分解実験を行った。酸化チタン薄膜をつけたガラス体の表面に紙で薄くサラダ油を 1 c m 2 当たり 0 . 1 ~ 0 . 1 5 m g になるよう塗布した。塗布量は塗布前後の重量測定により求めた。少なくとも 2 0 0 ~ 4 0 0 n m の光の一部を含む紫外線光の光をガラス体表面で 3 m W / c m 2 となるように設置して照射後、経過時間と重量変化量の関係を求めるため所定時間におけるガラ

ス体の重量を精密天秤で測定し、分解活性の指標とした。8 時間後の分解率で防汚性をランク付けした。A ( 9 0 ~ 1 0 0 % ) , B ( 7 0 ~ 8 9 % ) , C ( 5 0 ~ 6 9 % ) , D ( 4 9 % 以下 )

約 1 リットルの反応容器に所定のサンプルを設置し、所定量のたばこの煙を付着後、1 m W / c m 2 の紫外線を照射しながら、色差計にて色の変化を測定し、たばこのヤニの分解性を評価した。1 時間後の分解率で防汚性をランク付けした。A ( 9 0 ~ 1 0 0 % ) , B ( 7 0 ~ 8 9 % ) , C ( 5 0 ~ 6 9 % ) , D ( 4 9 % 以下 )

## 【 0 0 3 0 】 消臭機能測定法

約 1 . 5 リットルの反応容器に所定のサンプルを設置し、内部が 1 3 0 0 p p m の濃度になるようアセトアルデヒドガスを注入した後、1 . 2 m W / c m 2 の紫外線照射を行い、濃度減少により消臭機能を測定した。1 時間後の分解率で防汚性をランク付けした。A ( 9 0 ~ 1 0 0 % ) , B ( 7 0 ~ 8 9 % ) , C ( 5 0 ~ 6 9 % ) , D ( 4 9 % 以下 )

## 【 0 0 3 1 】 光直線透過率の測定

酸化チタンを付けたガラス体の一部を切断し幅 1 0 m m 、長さ 2 0 m m の試料を準備した。同様な試料を酸化チタンを付けていないガラス体で準備して、片方を試料側、片方を参照側として、島津製 U V - 3 1 0 0 P C 分光光度計により 5 5 0 n m の波長の光に対する直線透過率を測定した。

## 【 0 0 3 2 】 機械的耐久性測定法

密着性はセロテープ剥離試験、硬度は鉛筆硬度試験、磨耗性は消しゴム磨耗試験で行った。密着性および磨耗性は剥離しないもの、磨耗しないものを合格とした。

## 【 0 0 3 3 】 化学的耐久性試験法

耐沸騰水試験は J I S K 5 4 0 0 で、耐アルカリ試験は 0 . 0 5 % N a O H 水溶液を使用して J I S K 5 4

0 0 の方法に準じて 2 4 時間浸漬して試験した。

## 【 0 0 3 4 】

表 - 2

| 実施例 | 組成物<br>番号 | 焼成<br>温度 | 膜厚<br>(nm) | 透過率<br>(%) | 防汚性 | 密着性 | 硬度  | 耐煮<br>沸性 | 耐アル<br>カリ性 |
|-----|-----------|----------|------------|------------|-----|-----|-----|----------|------------|
| 7   | D - 1     | 500      | 100        | 85         | A   | 合格  | 6 H | 合格       | 合格         |
| 8   | D - 1     | 500      | 50         | 80         | B   | 合格  | 7 H | 合格       | 合格         |
| 9   | D - 1     | 650      | 150        | 90         | A   | 合格  | 6 H | 合格       | 合格         |
| 1 0 | D - 2     | 500      | 100        | 88         | A   | 合格  | 5 H | 合格       | 合格         |
| 1 1 | D - 3     | 600      | 50         | 70         | C   | 合格  | 7 H | 合格       | 合格         |
| 1 2 | D - 4     | 500      | 50         | 80         | A   | 合格  | 4 H | 合格       | 合格         |
| 1 3 | D - 5     | 550      | 200        | 75         | B   | 合格  | 6 H | 合格       | 合格         |

【 0 0 3 5 】 表 - 2 の結果より、実施例 7 の酸化チタン薄膜硝子は、可視光透過率 8 5 % 、防汚性 A ランク、鉛筆硬度 6 H 、及び密着性、耐沸騰水性、耐アルカリ性が合格であり、優れた光学特性、機械的耐久性、化学的耐久性有し、かつ、効率のよい防汚性の光触媒構造体であった。また、実施例 8 ~ 1 3 の酸化チタン薄膜硝子も、可視光透過率 7 0 % 以上、鉛筆硬度 4 H 以上、及び

た光学特性、機械的耐久性、化学的耐久性有し、かつ、効率のよい防汚性の光触媒構造体であった。

【 0 0 3 6 】 < 光触媒活性試験 > 実施例 7 、実施例 1 3 及び比較例 2 で作成した酸化チタン薄膜に関して、たばこのヤニの付着性、ヤニの分解性及びアセトアルデヒドの消臭性を比較し、表 - 3 に示した。

## 【 0 0 3 7 】

表-3

| 実施例                   | 1 3 | 7    | 比較例 2 |
|-----------------------|-----|------|-------|
| ゾル系酸化チタン<br>含量 (wt %) | 5.0 | 23.0 | 100   |
| 膜厚 (nm)               | 200 | 100  | 500   |
| 透明性                   | 透明  | 透明   | 白濁    |
| 密着性                   | 合格  | 合格   | 不合格   |
| 煙草ヤニの付着性              | 小   | 小    | 大     |
| 煙草ヤニの分解性              | B   | A    | A     |
| アセトアルデヒド<br>の消臭性      | C   | B    | A     |

【0038】比較例2の膜表面は非常に多孔質で表面積が大きく、煙草のヤニを吸着しやすく、ヤニの分解性やアセトアルデヒドの分解・消臭には適しているが、膜表面が白濁しており、膜の密着性も弱いので、光の透過性を必要とする用途や膜表面に手で接触したりする装置には使用できない。一方、実施例7および13では、汚れにくくかつ、付着した汚れは即座に分解できる自己浄化性を有し、かつ、透明で耐久性にも優れている。特に、

実施例7はそのバランスがよくとれた光触媒構造体である。また、これらの酸化チタン薄膜硝子は、通常の白色蛍光灯の光の元でも大腸菌に対する殺菌性があり、病院や食品産業などで有効に利用できるものであった。

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30 って、約200nmのアナターゼ型酸化チタン薄膜を成膜し、水銀灯用酸化チタン薄膜硝子を作成した。この酸化チタン薄膜硝子を高速道路照明用の前面硝子として用いて、従来の前面硝子と車の排気ガスによる汚れをトンネル内で4ヶ月間比較した。従来硝子を用いた方は、汚れもひどく、24%の照度低下が認められたが、酸化チタン薄膜を用いた硝子は、汚れも少なく、汚れによる照度低下は6%で、優れた防汚性を示した。

【0040】

【発明の効果】本発明の酸化チタン薄膜形成用組成物は、調製後安定に保存でき、また、本発明の酸化チタン薄膜形成用組成物を用いることにより優れた光触媒活性を有し、かつ、優れた光学特性、機械的耐久性及び化学的耐久性等、バランスのとれた酸化チタン薄膜光触媒構造体を提供でき、特に、高い透過率と、防汚性能が必要とされる屋外用照明器具に用いるに最適である。

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